INFLUENCE OF HIGH TEMPERATURE OVERHEATING TO MICROSTRUCTURE OF DEGRADED STEEL SUPER 304H

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Abstract

This paper documents the microstructure changes of steel SUPER 304H caused by high temperature overheating (1140 °C, 15 hours). The experimental material was firstly isothermally laboratory exposed about 30,000 hours at temperature 650 °C and then subject to high temperature overheating. Main focus was given to microstructural changes and precipitation processes. Paper summarized influence of those changes to practical applicability of steel SUPER 304H for ultra-super critical (USC) coal power plants. Base material, laboratory expose state and overheated state were compared. Combination of color etching and optical microscopy method, electron scanning microscopy and energy dispersive spectroscopy analysis was used for comparison.

Keywords: SUPER 304H, high temperature overheating, USC, sigma phase precipitation, microstructure changes

1. INTRODUCTION

The increment of coal power plants working parameters (steam temperature and pressure) is continuously process strongly influent by available construction materials. Systematic parameters increment is in connection with application of the new material modification or the new materials. Working conditions are at the edge of possible steel usage for the last generation of the USC or A-USC power plants.

General requirements for austenitic steel in the superheater application are sufficient creep resistance and mechanical properties, corrosion resistance and exfoliation resistance. Steels SUPER 304H is categorized like suitable for this type of application [1,2]. Producer of this steels are Nippon Steel & Sumitomo Metal Corporation and Manessman.

SUPER 304H is type 18/9 (18 wt. % chromium and 9 w. % nickel) complexly alloyed creep resistant austenitic steels. The alloying elements are added for improving steels creep resistance. Steel SUPER 304H is alloyed by (in wt. %) 0.4 Nb, 0.1 N and 3.0 Cu, carbon content is optimised at value of 0.1 wt. % [3]. It is possible to categorise this steel like complex alloyed. The relatively high content of an alloying elements leads to thermodynamically instability of steel. The instability means phase precipitations during thermal exposition.

Conditions for precipitation of the brittle sigma phases in austenitic steels are listed in literature [4] according its chemical composition. Steels SUPER 304H meet those conditions. Precipitation of the sigma phase is high possible. Sigma phase precipitation deteriorates steel mechanical properties. Results presented in literature [5,6] confirmed precipitation of the sigma phase for steel SUPER 304H under the heat exposition.

Changes of precipitated sigma phase caused by high temperature overheating are summarised by this paper.

2. METHODOLOGY PART

2.1. Experimental material

Specification of steel is listed in [7]. Material was supplied by the Sumitomo metals. Steel SUPER 304H was supplied in form of the seamless tubes with outer diameter 38 mm, wall thickness 6.3 mm and tube length of 5700 mm [7]. Heat treatment made by producer (Sumitomo) was solution annealing under conditions 1150 °C / 2 min. / cold by water quenched [7].

The heat number of supplied steel is F124139. Its chemical composition summarized **Table 1**. Supplied steel is in accordance with the standard ASME Case 2328-1 prescribed values.

Table 1 Chemical composition of supplied steel SUPER 304H [7]

(wt. %)	C	Si	Mn	P	S	Cu	Cr	Ni	Nb	B	N	Al
Min. (ASME Case 2328-1)	0.07	-	-	-	-	2.50	17.0	7.5	0.30	0.001	0.05	0.003
Max. (ASME Case 2328-1)	0.13	0.30	1.00	0.04	0.01	3.50	19.0	10.5	0.60	0.010	0.12	0.030
Heat No. F124139	0.08	0.25	0.81	0.003	0	3.07	18.3	9.0	0.49	0.004	0.11	0.005

Experimental material was isothermal laboratory exposed at temperature 650 °C by approximately 3×10^4 hours. Long-term laboratory isothermal exposition caused the sigma phase precipitation in SUPER 304H microstructure. After long-term isothermal exposition was performed high temperature overheating 1140 °C for 15 hours.

2.2. Experimental methods

Two types of etchants were used for selective and uniform etching:

- *Selective etching for the sigma phase revealed - Electrolytic etching with 10 % KOH in distilled water (2 V dc, 4 s)*
- *Uniform etching - Glyceregia [8] - HCl, glycerol, HNO_3 (ration 3:2:1). Applied by swabbing*

Documentation of the sigma phase was made by the optical microscope Nikon eclipse MA200 in magnification 1000 x. Image analysis was made in the software NIS-Elements Ar by automatic binary image detection with followed operator refinement.

SEM microscope used for microstructure observation and EDS analysis was Jeol JSM-7600F. Used acceleration voltage was in range 15 - 20 KV. Images were taken by SEI detector (secondary electrons).

Observation was focused to the particles at the grain boundaries. Phase analysis at the grain boundaries and inside grains was performed via EDS analysis. SEM was used for observation of the fraction surfaces to provide information about morphology of a fracture and particles identification.

SEM - EDS analysis was performed via the detector Oxford X-Max 50 mm^2 with operation software Inca. Chemical analysis provides information not just about constitution of the precipitates but also about surrounding area or chemical elements depleted zones. Last application of EDS analysis used in this paper was mapping of chemical composition.

The impact strength measurement was done by specifications in norm [9]. The reduced impact samples with 2 mm V notch and 5 mm width was used. Energy of the used Charpy pendulum hammer was 300 J.

3. EXPERIMENTAL PART

Table 2 summarise the sigma phase chemical composition and lattice parameters. Type 316-alloy is the most chemically similar alloy to SUPER 304H. According **Table 2** will have the sigma phase precipitate in SUPER 304H chemical constitution more than 30 wt. % of chromium and about 55 wt. % of iron.

Table 2 Chemical composition and lattice parameters of the sigma phase in various alloys [4]

Alloy	Lattice parameters (Å)	Composition of phase (wt. %)					Formula
		Fe	Cr	Ni	Mo	Si	
Fe-Cr	a_0 = 8.799, c_0 = 4.544						Fe-Cr
Fe-Mo	a_0 = 9.188, c_0 = 4.812						Fe-Mo
17Cr-11Ni-2Mo-0.4Ti	----		30	4.3	9	0.8	
17Cr-11Ni-0.9Mo-0.5Ti	----		33	4.5	5.4	0.7	
Type 316	a_0 = 8.28~8.38, c_0 = 4.597~4.599	55	29	5	11		$(FeNi)_x(CrMo)_y$
Type 316L	a_0 = 9.21, c_0 = 4.78						
20Cr-25-34Ni-6.5-8Mo	a_0 = 8.87, c_0 = 4.61	35 / 37	17 /2 6	15 /2 1	21 / 28		
25Cr-20Ni	----	40	46	9.4		3	

Sigma phase assist embrittlement of exposed steel SUPER 304H. The impact strength measurements at reduced width (5 mm) specimens with V notch were carried out. Experimental material was isothermally aged at 675 °C for 20,000 hours for sigma phase precipitation. Results are summarized in **Table 3**. [10]. Base material fracture surface (**Figure 1**) was ductile with no marks of brittle fracture. Fracture surface after exposition (**Figure 2**) was mostly brittle. This change is caused by the sigma phase precipitation. Sigma phase was identified by measuring of fracture surface particles chemical composition (**Figure 2**).

Table 3 Results of impact testing of SUPER 304 [10]

State	KV 300 / 5 (J)	The sigma phase area fraction (%)
Base material	44.7 ± 1.0	0.0
Exposed material	11.4 ± 0.4	2.6

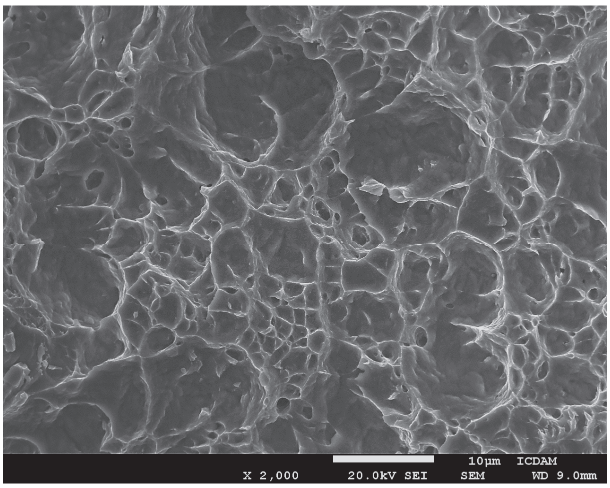

Figure 1 Ductile fracture surface of as-received SUPER 304H steel

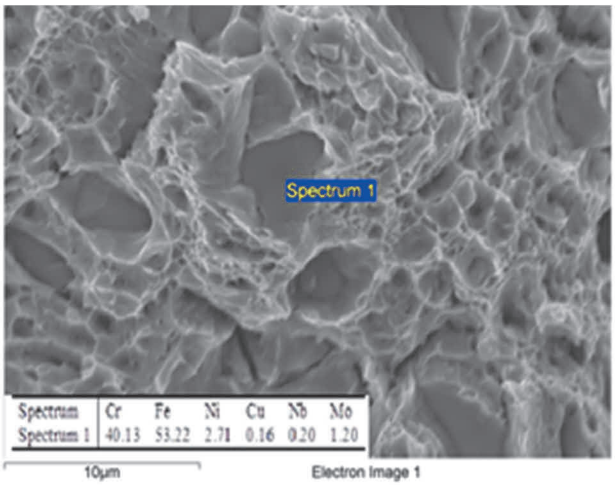

Figure 2 Fracture surface of exposed SUPER 304H steel with sigma phase [10]

Follow image (**Figure 3**) show direct comparison between electron microscope image, measured chromium map and optical microscope image. Red circles added to **Figure 3** connect one of the sigma phase displayed by different methods. Results documented by **Figure 3** gave possible to use optical microscopy for the sigma phase quantification.

Chemical composition of the sigma phase and SUPER 304H steel matrix summarise **Table 4**. In **Table 4** is highlighted chromium and iron content. Ration of chromium and iron for Spectrum 1 confirm sigma phase precipitation.

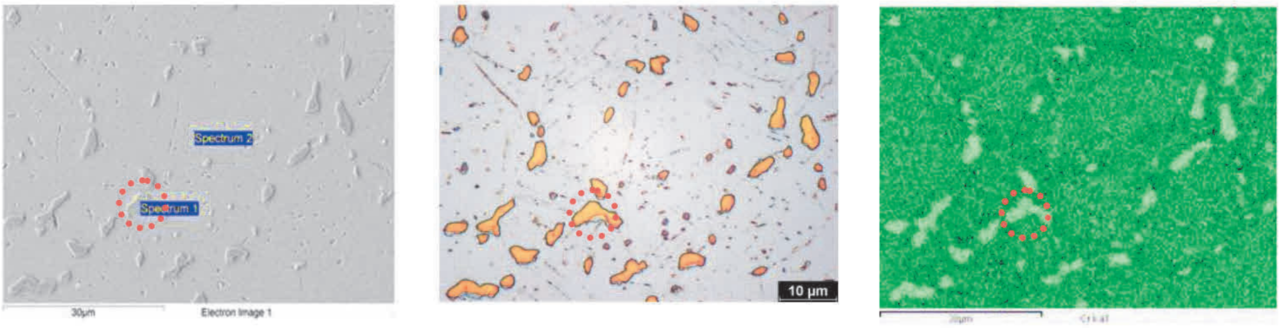

Figure 3 Comparative image for sigma phase verification for optical microscopy

Table 4 Chemical measurement results for **Figure 3**

Spectrum	Si	P	Ca	Cr	Fe	Ni	Cu	Nb	Mo	W
Spectrum 1 (wt.%)	0.97	0.46	0.35	36.29	56.27	3.33			1.98	0.35
Spectrum 2 (wt. %)	0.37			18.84	66.95	8.80	4.54	0.15	0.35	

Microstructure comparison between aged and high temperature overheated state give **Figure 4** and **Figure 5**. Microstructure of isothermally exposed sample (**Figure 4**) is in agreement with fracture surfaces documented by **Figure 2**. At the triple grain points precipitated sigma phase which deterioration mechanical properties. The main difference between compared states is dissolution of the sigma phase at triple grain points. Triple grain points are without documentable sigma phase for exposed (laboratory exposed at temperature 650 °C by approximately 3 x 10^4 hours) and high temperature overheated state (**Figure 5**). The mechanical properties should be improved by the sigma phase dissolving.

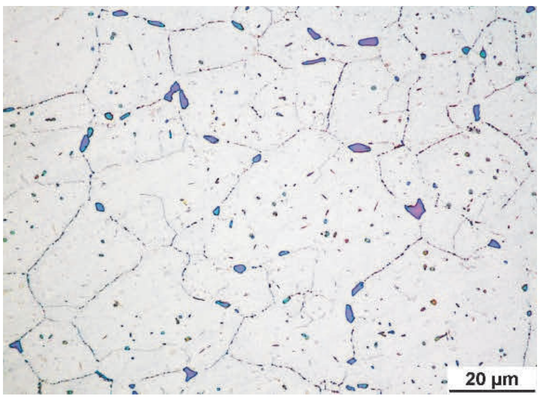

Figure 4 Isothermally exposed 650 °C / 2.45 x 10^4 sample before high temperature overheating

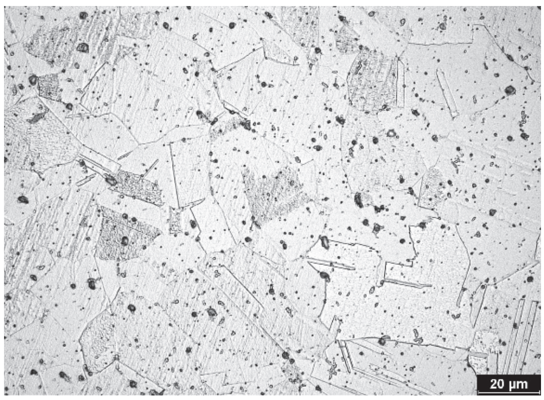

Figure 5 High temperature overheated sample

Resolution of the optical microscopy is lower in comparison with SEM. The sigma phase dissolution was confirmed used EDS chemical composition mapping. **Figure 6** shows from left to right electron image, mix chemical map and chromium content map. Particles highlighted at the chemical mix map by blue colour are niobium carbonitrides. Chromium content map confirm the sigma phase dissolving.

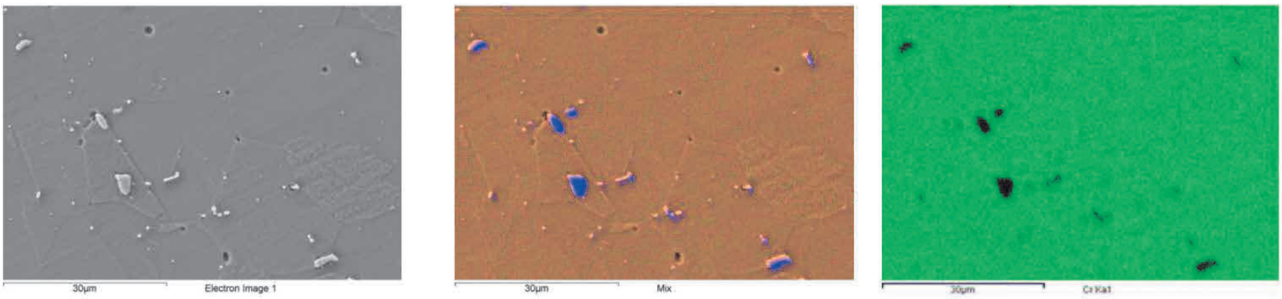

Figure 6 Chemical maps of high temperature overheated state

High temperature overheating started massive grain coarsening at the outer tube surface (**Figure 7**). Secondary grains colony are in some tube parts across whole tube wall thickness.

Figure 7 Tube wall cross-section macro image

4. DISCUSION AND CONCLUSION

Sigma phase verification was based on chemical composition measurement. Table 2 summarizes sigma phase nominal chemical composition for various alloys. According Table 2 will have the sigma phase precipitate in SUPER 304H chemical constitution more than 30 wt. % of chromium and about 55 wt. % of iron.

Absorb energy measurement shown significant decrease between base material and exposed state. Drop in absorb energy was by 75 %. Sigma phase was documented in exposed state samples. SEM analysis confirmed sigma phase precipitation at fracture surface. Drop of absorb energy was caused by brittle sigma phase precipitated in exposed material.

SUPER 304H brittleness will be serious application problem for USC power plants. Brittleness can cause unstable fractures during operation caused by superheater vibrations or cracking during repair welding.

The sigma phase embrittlement effect may be removing by dissolving annealing of exposed state. Sigma phase dissolve over 815 °C. Temperature 815 °C is valid for binary system Cr - Fe. Sigma phase precipitates in steel SUPER 304H contain substitutional elements. Substitutional elements shift the dissolving temperature to a higher value. Parameters of applied dissolving annealing were 1140 °C for 15 hours.

Annealing led to dissolution of the sigma phase. Dissolution was confirmed through optical microscopy and SEM. The sigma phase dissolution will solve the problem of SUPER 304H embrittlement.

Parameters of dissolving annealing (high temperature overheating) were at higher part of possible range. High temperature overheating can cause more than even sigma phase dissolving. Massive grains coarsening were documented for overheated state. Grains coarsening will lead to decreasing of creep resistance and problems with exfoliation. Grain coarsening is negative for USC application.

The sigma phase can be dissolve by application of high temperature dissolving annealing. Negative influence of annealing is grains coarsening. Application of shorter dissolving time can prevent grains coarsening. Future experiments will optimize annealing parameters for preventing grains coarsening.

ACKNOWLEDGEMENTS

This work was financially supported by the Technology Agency of the Czech Republic within the project no. TA01010181, by Ministry of Industry and Trade of the Czech Republic within the project no. FR-TI3/458, by Ministry of Education, Youth and Sport of the Czech Republic within the project no. LO1207, and by the Grant Agency of the Czech Technical University in Prague within the grant no. SGS 16/215/OHK2/3T/12.

REFERENCES

[1] VISWANATHAN, R., HENREY, J.F., TONZOSH, J., STANKO, G., SHINGLEDECKER, J., VITALIS, B., PURGERT, R. U.S. Program on Materials Technlogy for Ultra-Superctitical Coal Power Plant. *Jurnal of Materials Engineering and Performance,* 2005, vol. 14, pp. 281-292.

[2] WISWANATHAN, Vis, PURGERT, Robert and RAWLES, Patricia. Coal - fired power materials. *Advanced materials and processes,* 2008, no. 8, pp. 47-49.

[3] ABE, F., KERN, T.U., VISWANATHAN, R. *Creep-resistant steels*. England: Woodhead Publishing Limited and CRC Press LLC, 2008. p. 700.

[4] HSIEH, Ch.iCh., WU, W. Overview of Intermetallic Sigma (σ) Phase Precipitation in Stainless Steels. *ISRN Metallurgy,* 2012, pp. 1-16.

[5] HORVÁTH, L., ANDRŠOVÁ, I., PODHORNÁ, B., HORVÁTH, J. *Program MPO TIP „Materiálové řešení průmyslových zařízení pracujících s ultrapřehřátou parou“ Zpráva o průběhu řešení za rok 2014*. Prague: UJP PRAHA a.s., 2014. 187 p.

[6] JI, Y. Su, PARK, J., LEE, S.Y., KIM, J.W., LEE, S. Mo., NAM, J., HWANG, B., SUH, J. Y., SHIM, J. H. Long-term evolution of σ phase in 304H austenitic stainless steel: Experimental and computational investigation. *Materials Characterization*, 2017, vol. 128, pp. 23-29.

[7] *Inspection certificate: Super 304H - heat no. F124139*. Japan: Sumitomo Metals, 2011. 6 p.

[8] *Buehler Sum - Met the science behind materials preparation; a guide to materials preparation and analysis*. Lake Bluff Il: Buehler, 2004. 76 p.

[9] *ČSN EN ISO 148-1: Metallic materials - Charpy pendulum impact test - Part 1: Test method*. Prague: ÚNMZ, 2007. 32 p.

[10] HORVÁTH, J., JUNEK, M., JANOVEC, J. The Changes in Mechanical Properties of Austenitic Creep Resistant Steels SUPER 304H and HR3C Caused by Medium-term Isothermal Ageing. *Solid State Phenomena,* 2017, vol. 258, pp. 639-642.